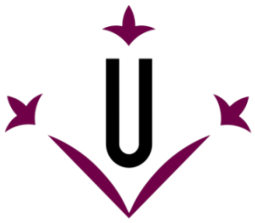

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Antimony speciation in aqueous solution followed with AGNES

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Abstract

Determining antimony speciation is essential to understand its environmental behaviour and potential (eco)toxicological effects. Absence of Gradients and Nernstian Stripping Techniques (AGNES) is an electroanalytical technique that has been applied up to date to the determination of the free metal ion concentrations of Zn(II), Cd(II), Pb(II) and In(III). In this work, the first application of AGNES to the measurement of the concentration of one particular species of Sb(III) in aqueous solution is developed. The extensive hydrolysis of this element, even at low pH, suggests the convenience of performing calibrations and AGNES measurements in terms of the $Sb(OH)_{3(aq)}$ concentration, rather than the "free" ion. A new preconcentration factor, *Y'*, is also introduced as the ratio between $[Sb^0]$ in the amalgam and $[Sb(OH)_{3(aq)}]$ in the solution. *Y'* dependence on pH is evaluated with calibrations at different pH values. The experimental values of $Sb(OH)_{3(aq)}$ obtained with AGNES in the titration of antimony with the organic ligand oxalate agree very well with the values predicted with the

complexation constants recently reported. This promising methodology opens the way to tackle antimony speciation with AGNES in other systems.

Keywords: AGNES, Sb, speciation

1. Introduction

Antimony has four different oxidation states: -III, 0, +III and +V. In the environment, it is mainly found as Sb(III) and Sb(V). The prevalence of one or another redox state depends on the medium: while Sb(V) predominates in oxygenated systems, Sb(III) does in non-oxygenated ones. Although spectroscopic techniques have been developed to elucidate Sb redox states [1], there is still the need to develop approaches relying on smaller, less expensive equipment and with the prospect of an *in situ* application. Thus, electroanalytical approaches [2, 3] can also contribute to this endeavour. Electroanalytical techniques, and especially Anodic Stripping Voltammetry (ASV), have been reported to distinguish between Sb(III) and Sb(V) [4, 5]. Adsorptive Stripping Voltammetry (AdSV) and Potentiometric Stripping Analysis (PSA) have also been used. Mercury electrodes, either the Hanging Mercury Dropping Electrode (HMDE) or the Mercury Film Electrode (MFE), have been the most frequently chosen ones with limits of detection that reach in some studies subnanomolar concentrations. Speciation Sb(III)/Sb(V) is based on the lack of activity of Sb(V) at the mercury electrode, except in highly acidic or halidic electrolyte medium. Potentiometry with Ion Selective Electrodes (ISE) is also an alternative, but the reported limits of detection are considerable higher (not lower than submicromolar). Very complete reviews on various aspects of Sb [5-7] have been published.

Absence of Gradients and Nernstian Stripping Technique (AGNES) [8, 9] is a particular case of an anodic stripping voltammetry technique. It is based on the reduction of the analyte in solution and its accumulation in the electrode until reaching a special situation of lack of concentration gradients and Nernstian equilibrium, followed by a stripping stage, where the analytical signal is recorded. With the AGNES technique, the free metal concentration can be directly determined. Free Zn, Cd and Pb concentrations have been measured in sea [10, 11] estuarine [12] and river waters [13] in soil extracts [14], in systems containing humic acids [15, 16] or nanoparticles [17-21] and in wine [22], among others. Although the analyte in all these applications was a divalent ion, the detection of the free concentration of a trivalent metal, In, with AGNES has also been recently reported [23, 24].

The aim of this article is to demonstrate the suitability of AGNES technique to follow the speciation in solutions containing antimony (III). Some specific challenges have to be considered, such as the hydrolysis phenomena. In this work, the speciation analysis of antimony with AGNES in synthetic solutions containing only Sb and Sb in combination with an organic ligand (oxalate) is tackled.

2. Materials and Methods

2.1 Equipment and Reagents

Potassium nitrate (Suprapur, Merk, Germany) solution was used as the inert supporting electrolyte to obtain an ionic strength of 0.1 mol L^{-1}. Nitric acid (Fluka, Germany), potassium hydroxide (Fluka, Germany) and hydrochloric acid (Merck, Germany) were used to adjust the pH. Sb_2O_3 (Merck, Germany) was used to prepare antimony solutions as specified in the next section and a commercial Sb solution 1000 mg L^{-1} in 2 mol L^{-1} HCl (Merk, Germany) was employed to standardise them.

Ultrapure water (Milli-Q plus 185 System, Millipore) of 18 MΩ cm resistivity was employed in all the experiments. Purified water-saturated nitrogen N_2 was used for deaeration of solutions.

Voltammetric measurements were carried out using an Eco Chemie Autolab PGSTAT 12 potentiostat attached to a Metrohm 663 VA Stand and to a computer by means of the GPES 4.9 (Eco Chemie, the Netherlands) software package. The working electrode was a Metrohm multimode mercury drop electrode. Drop size 1, which according to the catalogue corresponds to a radius of r_0= 1.41×10^{-4} m, was used in AGNES measurements. The auxiliary electrode was a glassy carbon electrode and the reference electrode was Ag | AgCl | KCl (3 mol L^{-1}) encased in a 0.1 mol L^{-1} KNO_3 jacket (ref. 6.0726.100 from Metrohm).

A glass combined electrode (Hach 52 09) was attached to an Orion Dual Star ion analyser (Thermo) and introduced sporadically in the cell to control de pH. A glass jacketed cell provided by Metrohm, thermostated at 25.0ºC, was used in all the experiments.

To filter Sb_2O_3 solutions, membrane filters of mixed cellulose ester with a mesh of 0.45 μm were employed (Scharlau, Germany).

For oxalate solutions, potassium oxalate monohydrate (p.a. Fluka, Switzerland) was employed.

2.1.1 Preparation of standard antimony solutions

Solid Sb_2O_3 was dispersed in Milli-Q water and the pH was adjusted to 2 with HNO_3. After stirring overnight, the dispersion was filtered (0.45 μm). The filtrate was taken to a volume with Milli-Q water and, then, the pH was finally checked (and fixed to 2, if

necessary). All this preparation (except filtration) of the $Sb(OH)_3$ stock solution was performed under N_2 atmosphere to avoid conversion to Sb(V).

The methodology reported by Quentel and Filella [4] was followed to determine Sb(III) at HCl 0.5 mol L^{-1} and total Sb at HCl 5 mol L^{-1} with Differential Pulse Anodic Stripping Voltammetry (DPASV) technique. DPASV was applied with drop size 3 in the Metrohm stand (which corresponds to a drop area of 0.52 mm^2) applying a deposition potential of -0.45V for 30 s, with a stripping step from -0.45 V to -0.1 V (for 0.5 mol L^{-1} HCl) or from -0.45 V to -0.2 V (for 5 mol L^{-1} HCl), with a step potential of 2 mV and a modulation amplitude of 20 mV.

The stock antimony solutions prepared as described above were standardized following the standard addition method resulting in $c_{T,Sb}$= 2.7×10^{-5} M and 2.6×10^{-5} M. A dilution of the commercial 1000 mg L^{-1} Sb in 2 mol L^{-1} HCl standard was used for the additions in this procedure. The methodology of Quentel and Filella [4] was also applied for this 1000 mg L^{-1} standard in HCl indicating that all the Sb was in Sb(III) state. The total concentration in the Sb solution was also checked by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), confirming the total Sb concentration value obtained by DPASV with a difference less than 0.5%.

2.2 Procedures

Absence of Gradients and Nernstian Equilibrium Stripping technique (AGNES) consists in two stages [8]. In the first stage, a potential is applied to reduce the analyte (a metal in previous work) and amalgamate it with the mercury electrode until reaching flat concentration profiles and Nernstian equilibrium conditions. We call gain or preconcentration factor, *Y*, to the ratio of concentrations at both sides of the electrode surface

$$Y = \frac{\left[\mathrm{M}^0\right]}{\left[\mathrm{M}\right]} = \exp\left[-\frac{nF}{RT}\left(E_1 - E^{o\,\prime}\right)\right] \quad (1)$$

where $[M^0]$ is the homogeneous concentration of reduced analyte in the amalgam by the end of the first stage, [M] is the free concentration (of analyte) in the bulk solution, *n* is the number of exchanged electrons, *F* is the Faraday constant, *R* the gas constant, *T* the temperature, E_1 the applied deposition potential and $E^{0\prime}$ the standard formal potential of the redox couple. The relationship between the gain and the deposition potential can be obtained from an ancillary DPP [8]

$$Y = \sqrt{\frac{D_{\mathrm{M}}}{D_{\mathrm{M}^0}}}\exp\left[-\frac{nF}{RT}\left(E_1 - E_{\mathrm{peak}} - \frac{\Delta E}{2}\right)\right] \quad (2)$$

The aim of the second stage of AGNES is the quantification of the analyte accumulated in the amalgam. Different variants have been suggested for the second stage [25, 26]. AGNES-I consists in applying a constant reoxidation potential leading to diffusion limited conditions and measuring the current at a certain stripping time, while in AGNES-Q the charge is obtained from the integration of the stripping current. In AGNES-LSV the stripping current is recorded while the potential is scanned from E_1 to more positive values. In AGNES-SCP the evolution of the potential is recorded while a fixed stripping current, I_s, is kept, so that the charge can be obtained from the transition time, τ, which is the time required for the complete reoxidation. The faradaic charge can be computed with the expression [27]

$$Q = \left(I_s - I_{\mathrm{Ox}}\right)\tau \quad (3)$$

where I_{Ox} is the charge due to other oxidants and is estimated from the intensity current at the end of the deposition stage (without stirring), called “waiting stage” whose duration is represented as t_w.

Either the current or the charge can be related to the concentration of amalgamated metal and, also, to the analyte concentration in the solution. For the charge

$$Q = nFV_{\mathrm{Hg}}\left[\mathrm{M}^0\right] = nFV_{\mathrm{Hg}}Y\left[\mathrm{M}\right] = \eta_{\mathrm{Q}}Y\left[\mathrm{M}\right] \quad (4)$$

where Q is the faradaic charge, V_{Hg} is the volume of the mercury electrode and η_{Q} is the normalized proportionality factor.

If we consider the analysis in a solution containing antimony, eqn. (1) can be expressed as

$$Y = \frac{\left[\mathrm{Sb}^0\right]}{\left[\mathrm{Sb}^{3+}\right]} = \exp\left[-\frac{nF}{RT}\left(E_1 - E^{o\,\prime}\right)\right] \quad (5)$$

Taking into account the high level of hydrolysis of Sb(III), it might be unrealistic (or at least, unsuitable) to continuously work in terms of the elusive species Sb^{3+}. According to VMINTEQ 3.1 [28] with its default database, even at pH 2, the main antimony species in solution is $Sb(OH)_{3(aq)}$ (from now on we will omit this subscript "aq"), so we develop the reporting of AGNES speciation results in terms of $[Sb(OH)_3]$ instead of $[Sb^{3+}]$. The reduction reaction that takes places in the electrode surface can, then, be written as

$$\mathrm{Sb(OH)_3} + 3\mathrm{H^+} + 3e^- \rightleftharpoons \mathrm{Sb^0} + 3\mathrm{H_2O} \quad (6)$$

$[Sb^{3+}]$ is related to $[Sb(OH)_3]$ through

$$\left[\mathrm{Sb(OH)_3}\right] = K_3\gamma_3\left[\mathrm{Sb^{3+}}\right]\left\{\mathrm{OH^-}\right\}^3 \quad (7)$$

where K_3 is the thermodynamic stability constant for $Sb(OH)_3$ and γ_3 is the activity coefficient for Sb^{3+} at the working ionic strength. Hence, we can define a new preconcentration factor, *Y'*, (the added prime is also a reminder of the pH dependence of this gain):

$$Y' \equiv \frac{\left[\mathrm{Sb}^{0}\right]}{\left[\mathrm{Sb(OH)_3}\right]} = \frac{Y}{K_3 \gamma_3 \left\{\mathrm{OH}^{-}\right\}^3} \quad (8)$$

Then, eqn. (4) can be written as

$$Q = \eta_Q Y \left[\mathrm{Sb}^{3+}\right] = \eta_Q Y' \left[\mathrm{Sb(OH)_3}\right] \quad (9)$$

which relates the measurable charge Q with the concentration of $Sb(OH)_3$.

3. Results and discussion

3.1 AGNES strategies for Sb determination

3.1.1 Deposition potentials

One of the first steps in implementing AGNES for a new element is to check whether equilibrium conditions are effectively reached for sufficiently long deposition times at certain deposition potentials [8, 29, 30]. The selection of suitable deposition potentials (E_1) is critical for AGNES, because too low gains yield low unreliable analytical signals, but too high gains would require too long deposition times to reach equilibrium. To compute deposition potentials linked to desired gains for antimony, we could not rely on the DPP relationship between Y and E, given by eqn. (2) as previously done for Zn, Pb and Cd. In our pH conditions, Sb is mainly hydrolysed to $Sb(OH)_3$ so that the DPP peak position is very much affected by the thermodynamics and kinetics of $Sb(OH)_3$ dissociation and its reversibility at the electrode surface, so that, for accurate calculations, much involved expressions would be needed (where the values of some parameters are likely to be unavailable). Here, the strategy followed to initially choose the deposition potentials consisted in using Pb (a reversible metal extensively checked with AGNES [31]) as a reference. A DPP was applied in a solution containing only lead and at the same ionic strength of 0.1 M KNO_3. Also DPASV for Sb and Pb were run.

Taking into account the DPP peak potential for lead and the difference between DPASV peak potentials, a virtual DPP peak potential for antimony was estimated, from which a rough gain for Sb could be determined. We call Y_{nom} to this gain estimated taking Pb as reference. Y_{nom} was just used as a provisional value for the gains, thus enabling the checking of the required proportionality between charge (at equilibrium) and gain, until accurate gains were available from calibrations. Amongst the possible variants to quantify the accumulated Sb^0, AGNES-I was not the first candidate strategy because of the proximity of the end of Sb^0 reoxidation (around -60 mV in Fig 1) with mercury reoxidation (in solutions with complexants of Hg(I) such as chloride) and the need of a reoxidation potential E_2 well in diffusion limited conditions. So, AGNES-Q, with a constant reoxidation potential, was first evaluated.

Taking into account that the reoxidation peak for DPASV signals in a solution of antimony without any added ligand (see Fig. 1) is practically finished at -60 mV, a reoxidation potential E_2 of -60 mV was selected for the stripping stage of AGNES-Q. As seen in Fig 2, the evolution of the stripping current with time in the reoxidation stage shows a very slow decay. Note that with other elements, a typical stripping time of 50 s is usually sufficient for completely emptying the amalgamated analyte. This immediately indicates that diffusion limited conditions for reoxidation do not apply at this E_2, because of its being not sufficiently positive and/or a “sluggish stripping” (previously reported in solutions with large analyte concentration [32]) occurring, linked to some kinetic limitations. So, at this E_2, it is clear that AGNES-I cannot be applied.

In the variant AGNES-Q, the stripping charge can be computed by integration of the faradaic current with time:

$$Q = \int_0^{t_2} I\, dt \tag{10}$$

In AGNES-Q, one has to check that the integration time is sufficiently long so as to take into account the complete stripping of Sb^0 from inside the drop. Just by observing in Fig 2 that the stripping current is still decaying at 50 s, one suspects that integrating up to t_2= 50 s might be insufficient.

The attainment of AGNES equilibrium is usually seen as a plateau (or horizontal stabilization) in a "trajectory" (or time-series course), where the analytical signal (charge, in the case of AGNES-Q) is plotted against increasingly long deposition times and a fixed gain. Trajectories for four different gains are shown in Fig. 3: either with an integration time of 50 s (panel a) or with an integration time of 200 s (panel b). For 50 s integration time, the charge in the trajectory initially increases (this is expected), but, then, instead of stabilizing at longer and longer times, it begins to decrease. This evolution cannot be explained within the typical monotonous accumulation-towards-equilibrium scheme. We ascribe this decrease of the charge for long times to an insufficient integration time. Indeed, extension of the integration time to 200 s (in this example) is enough for emptying the drop and, as a consequence, the expected plateau at longer times is reached for each gain. The attainment of Nernstian equilibrium is also confirmed from the observed proportionality between the stabilized charges and the applied gains in Fig 3b. As previously indicated, larger gains required longer deposition times to reach the plateau: for instance, in Fig. 3b, 1600 s were needed for Y_{nom}=10, but just 800 s were sufficient for Y_{nom}=5. We conclude that AGNES-Q can be an alternative to measure $Sb(OH)_3$ in solution, but using longer stripping times than usual and taking care of choosing a suitable integration time. However, the use of very long integration times introduces a loss in the reproducibility due to the oscillations in the stripping currents (likely due to natural convection). So, and also in order to seek for shorter experimental times, another variant of AGNES was also evaluated.

3.1.2 Application of the variant AGNES-SCP

AGNES-SCP experiments at different deposition potentials (corresponding to different gains) and with increasing deposition times were also performed to a solution with a total concentration of antimony 1.5 μmol L^{-1}, 0.1 mol L^{-1} KNO_3 and at a pH fixed to around 2. The prescribed stripping current was 1 nA. The faradaic charge was computed with eqn. (3) [27] taking a value of I_{Ox} of -0.44 nA (obtained from the average value of the currents at the end of some sampled waiting stages).

In the trajectories (with replicates) of Fig. 4a, the charge obtained with AGNES-SCP is plotted *vs* deposition time, exhibiting the typical asymptotical approach towards equilibrium. The reported *Y'* values in the figure were obtained from a calibration (see section 3.2 below). As in the previous trajectories with Q-AGNES (Fig 3b), also in Fig 4a larger *Q* were obtained for larger gains and the time to equilibration is longer for larger *Y'*. These trajectories can be normalized to visualize these dependences with the gain, by dividing both *Q* and t_1-t_w by *Y'*, see Figure 4b. This kind of normalization has been previously applied in several works [23, 24]. The observed collapse of the plateaux of the different trajectories at the different gains in Fig. 4b confirms the Nernstian behaviour, as expected from the proportionality between (equilibrium) charge and gain in eqn. (9) and AGNES principles. The normalization of the time can be justified from the (approximate) functional dependence of the accumulated M^0 with deposition time [9]. In 4b, one sees that all normalized trajectories reach the normalized plateau at around an abscissa of 30 s, which suggest

$$t_1 - t_w = 30\ Y' \qquad (11)$$

as a rule to estimate the minimum time to reach equilibrium when measuring Sb at pH 2 with drop size 1 in HMDE. In previous works, using also the smallest drop size in the HMDE electrode and the maximum stirring rate in the stand, with Pb, Cd or Zn, the rule was t_1 - t_w=7 Y (Galceran2010) and with In it was t_1 - t_w=10Y [23]. It must be

highlighted that the values cannot be directly compared (as for Pb, Cd and Zn we used *Y*, while for Sb, *Y*' applies). It has also to be pointed out that an increase in time to reach equilibrium could be attributed to a lower diffusion coefficient of $Sb(OH)_3$ and/or electrodic irreversibility and/or homogeneous-kinetics factors.

Given the low solubility of antimony in mercury, there might be a problem (like the one described for high concentrations of Zn and Cd in solution[32]) if the concentration of Sb^0 in the amalgam was too high. The crossing or not of the solubility threshold can be easily decided. For instance, in the AGNES-SCP trajectories in Fig. 4, $[Sb(OH)_3]$ was 2×10^{-6} mol L^{-1} and *Y*' from 5 to 20, so that, through (8), the concentration of antimony amalgamated with mercury in the drop electrode $[Sb^0]$ ranges from 1×10^{-5} to 4×10^{-5} mol L^{-1}. These values are lower than the solubility of antimony in mercury reported by Verplaetse *et al* at 25 ºC [33] of 8.57×10^{-4} mol L^{-1} . If the predicted $[Sb^0]$ was higher than the solubility, one always has the possibility of working with lower *Y*', because there will be a range of $[Sb^0]$ (e.g. from 1×10^{-5} to 4×10^{-5} mol L^{-1}) where the analytical signal can still be large enough to be above the noise.

3.2 Calibrations

In order to determine $[Sb(OH)_3]$ in a sample from the measured charge obtained with AGNES (eqn. (9)), one needs to know η_Q and *Y'*.

For Zn, Cd and Pb [25], the ancillary technique DPP has been used to determine the preconcentration factor that corresponds to an applied potential, while η_Q is obtained from a calibration plot (*Q vs* [M]).

When the gain cannot be independently found (e.g. from a DPP peak) due to reasons such as a non fully-reversible or a highly hydrolysed system, an alternative, recently

introduced when working with In [23], can be adopted. This strategy (implemented also here) starts with the assumption that η_Q is known, 0.0034 C L mol^{-1} (computed from eqn (4) and taking the radius of the electrode as the one specified in the catalogue, 141 μm for drop 1). Then AGNES is applied to solutions with known [$Sb(OH)_3$] with a fixed deposition potential (called E_{calib}) and sufficiently long deposition times. From the slope of the plot (equilibrium) Q vs. [$Sb(OH)_3$] one can find, through (9), the gain applied during the calibration (called Y'_{calib}). Once we know the gain, Y'_{calib}, that corresponds to a potential, E_{calib}, from eqs (5) and (8), we can easily derive an expression to find the gain for any other given potential (or *vice versa*)

$$E_j = E_{calib} - \frac{RT}{3F}\ln\left(\frac{Y'_j}{Y'_{calib}}\right) \quad (12)$$

Fig. 5 shows the calibration plot Q *vs* [$Sb(OH)_3$] corresponding to AGNES-SCP experiments at pH = 2 in the range 4.4×10^{-7} mol L^{-1} to 2.9×10^{-6} mol L^{-1} $Sb(OH)_3$. [$Sb(OH)_3$] is calculated by inputting the total Sb and KNO_3 concentrations in the speciation program VMINTEQ with its standard database. At each calibration point, three experiments at the same deposition potential, but at three different deposition times (100 s, 200 s and 300 s) were performed to check the fulfilment of AGNES conditions. The linearity in Fig. 5 confirms the applicability of the AGNES-SCP technique to determine [$Sb(OH)_3$]. From the slope of the calibration, we calculated that a Y'_{calib} =3.64 corresponded to the applied potential E_{calib} = -0.190 V.

Similarly, a linear calibration plot has also been obtained with the variant AGNES-Q at pH = 2.

With other elements (e.g. Zn, Cd, Pb and In), the gain Y did not depend on the pH, so that one could calibrate at one pH and measure at another pH [17]. Now, with Sb, the dependence of Y' on pH hinders such direct transfer. However, it might be inconvenient

317 to have to calibrate always at the exact pH of each measurement, as sometimes there are
318 small pH variations in unbuffered (and even buffered) solutions. We start by deriving an
319 expression relating the *Y*' at two different pHs.
320 Eqn. (8) can be rewritten as a function of pH

321 $$Y' = \frac{\left[\mathrm{Sb}^0\right]}{\left[\mathrm{Sb(OH)_3}\right]} = \frac{Y}{K_3\gamma_3\left\{\mathrm{OH^-}\right\}^3} = \frac{Y}{K_3\gamma_3 10^{3(\mathrm{pH}-14)}} = \frac{Y\,10^{42-3\mathrm{pH}}}{K_3\gamma_3} \quad (13)$$

322 Dividing *Y*' for two solutions at different pH values (pH_1 and pH_2), but with the same
323 ionic strength and recalling the definition of *Y*' given by eqn. (8)

$$\frac{Y'_{\mathrm{pH_1}}}{Y'_{\mathrm{pH_2}}} = \frac{\exp\left[-\frac{3F}{RT}\left(E_{1,\mathrm{pH_1}} - E^{o\prime}\right)\right]}{\exp\left[-\frac{3F}{RT}\left(E_{1,\mathrm{pH_2}} - E^{o\prime}\right)\right]} \frac{10^{42-3\mathrm{pH_1}}}{10^{42-3\mathrm{pH_2}}}$$

324 Sb17f(14)
325
Taking decimal logarithms

326 $$\log\left(\frac{Y'_{\mathrm{pH_1}}}{Y'_{\mathrm{pH_2}}}\right) = \frac{3F}{RT}\left(E_{1,\mathrm{pH_2}} - E_{1,\mathrm{pH_1}}\right)\log e + 3\left(\mathrm{pH_2} - \mathrm{pH_1}\right) \quad (15)$$

327
which, at 25ºC, can be expressed as

328 $$E_{1,\mathrm{pH_2}} = E_{1,\mathrm{pH_1}} + \frac{0.059}{3}\log\left(\frac{Y'_{\mathrm{pH_1}}}{Y'_{\mathrm{pH_2}}}\right) - 0.059\left(\mathrm{pH_2} - \mathrm{pH_1}\right) \quad (16)$$

329 This equation can be used to compute the needed deposition potential at pH_2, for a
330 desired gain $Y'_{\mathrm{pH_2}}$, from the couple $Y'_{\mathrm{pH_1}}$ and $E_{1,\mathrm{pH_1}}$ corresponding to the gain and
331 deposition potential at another pH.
332
333 Conversely, once *Y*' has been determined from a calibration at a given pH, one can
334 directly compute *Y*' for an applied $E_{1,\mathrm{pH_2}}$ at a different pH (from the one of the
335 calibration):

$$Y'_{pH_2} = Y'_{pH_1} 10^{\frac{-3}{0.059}\left(E_{1,pH_2} - E_{1,pH_1} + 0.059(pH_2 - pH_1)\right)} \quad (17)$$

To check the validity of this expression, we have calibrated at two different pH values: 2.0 and 2.5. The calibration at pH 2.0 was performed with a deposition potential $E_{1,pH_1} = -0.195\ V$ and the Y'_{pH_1} resulted in 4.52, while for the calibration at pH 2.5 a slightly more negative potential $E_{1,pH_2} = -0.225\ V$ was applied and the Y'_{pH_2} was 3.80. The expected value of Y'_{pH_2} according to eqn. (17) differs 21% from the experimental one coming from its calibration at pH 2.5. Taking into account the intrinsic error in any AGNES measurement, eqn. (16) can be considered as a useful tool for sparing calibrations at all used pH values.

3.3 Complexation of Sb with oxalate

An experiment has been performed to check the suitability of AGNES to perform speciation measurements in presence of a ligand, here, oxalate. The concentration of $Sb(OH)_3$ measured with AGNES in a synthetic system containing Sb, oxalate and KNO_3 was compared to that predicted taking into account the constants for the system Sb – oxalate found in the literature. Tella and Pokrovski [34] reported the formation of a specie $Sb(OH)_2Oxa^-$:

$$Sb(OH)_3^0 + HOxa^- \rightleftharpoons Sb(OH)_2\,Oxa^- + H_2O \quad (18)$$

with log *K* = 3.8±0.2 at 20ºC and $\Delta_r H^0 = -37 \pm 30\ KJ\ mol^{-1}$

and also of $Sb(Oxa)_2^-$ specially relevant at higher oxalate concentrations

$$Sb(OH)_3^0 + 2HOxa^- \rightleftharpoons Sb(Oxa)_2^- + OH^- + H_2O \quad (19)$$

with log K = -5.9±0.1 at 20ºC and $\Delta_r H^0 = -19 \pm 10\ KJ\ mol^{-1}$

A 0.1 mol L^{-1} KNO_3 solution with a fixed amount of total antimony was introduced in the voltammetric cell and was titrated with additions of oxalate. AGNES-SCP was applied (initially and after each addition) with a deposition potential corresponding to gains in the range *Y*' from 2 to 10 (higher gains at lower concentrations) and with a stripping current of 1 nA. Circle markers in Figure 6 represent [$Sb(OH)_3$] experimentally obtained for different replicated experiments, while the continuous line corresponds to the values obtained with VMINTEQ 3.1 with the constants for Sb-oxalate complexes reported in [34]. The plot shows the good agreement between the experimental values and the predicted ones. The results obtained with AGNES also confirm the stability constants reported in the literature for the system Sb-oxalate.

4. Conclusions

The first implementation of AGNES to the speciation of a metalloid has been described here. The large hydrolysis leads to the introduction of a new gain, *Y*', relating the concentrations of Sb^0 in the amalgam and of $Sb(OH)_3$ in solution, see eqn (8), so that [$Sb(OH)_3$] is the retrieved information (rather than the "free" Sb^{3+}).

The variant AGNES-Q yields acceptable results, but very long stripping times need to be integrated due to some kind of sluggish stripping (see Figs 2 and 3). The variant AGNES-SCP is faster.

From the collapse of trajectories (Fig 4), one derives the rule (eqn (11)) that the deposition time (in seconds) has to be 30 times the applied gain. The gain for a certain temperature, ionic strength and pH can be obtained from a calibration, where the volume factor η_Q is taken as a known constant. If there was some inaccuracy in the assumed value of η_Q, it would impact on the computed *Y*', but this impact would cancel out when the fundamental eqn (9) was applied again with the sample data. The pH dependence of *Y*' does not necessarily implies the need of a calibration at each of the

working pH values, since there are expressions (eqns (16) and (17)) enabling the transfer of the calibrations from one pH to another. Contrary to *Y*, *Y'* does not change with the ionic strength.

This methodological extension of AGNES has been applied to Sb solutions at pH 2 and 2.5 and checked following $[Sb(OH)_3]$ upon oxalate additions (see Fig 6). Further work at higher pH is needed, as well as checking the stability constants of many other Sb(III) compounds whose values are uncertain[35].

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Figures

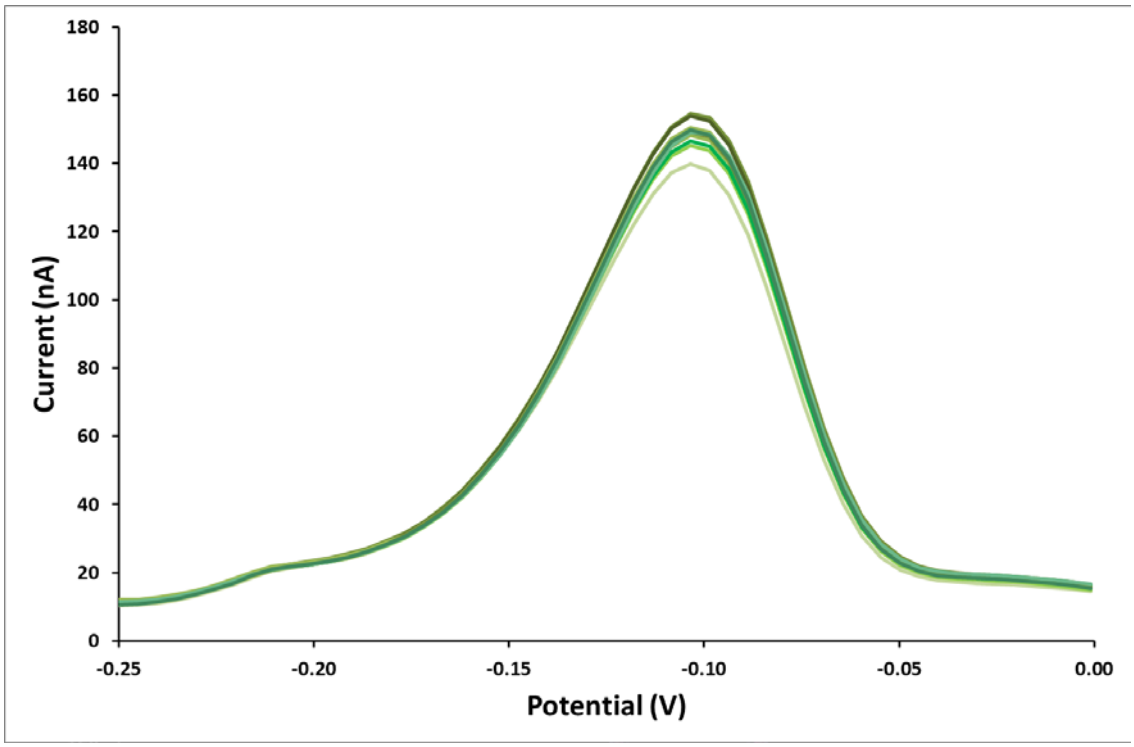


Figure 1. Differential Pulse Anodic Stripping Voltammograms of a Sb solution with a total antimony concentration of 1×10^{-4} mol L^{-1}, at pH 2.034 and 0.1 mol L^{-1} KNO_3. Deposition time was 30 s, deposition potential -0.3 V, and drop size 3.

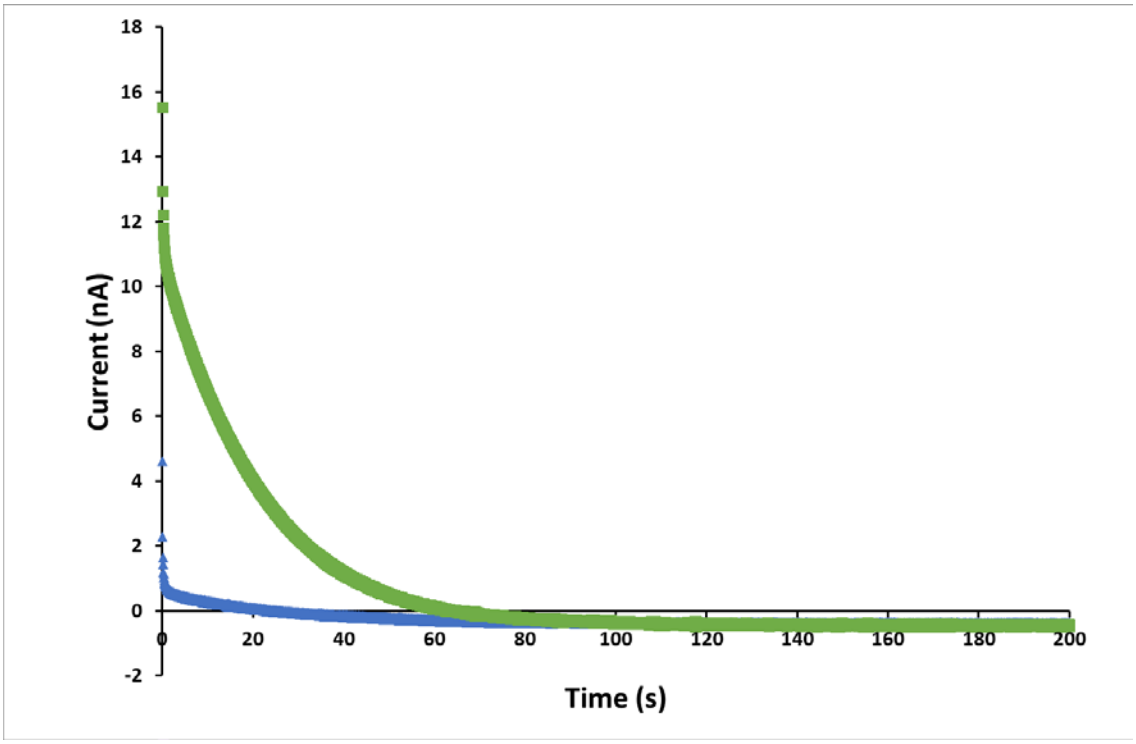


Figure 2. Plot of the current vs. stripping time t_2 from an AGNES-Q experiment, showing the slow emptying of Sb^0 from the drop along the reoxidation stage. Total antimony concentration 5×10^{-7} mol L^{-1} and pH = 2.053. Marker blue triangle: $Y_{nom} = 2$, $E_1 = -0.2253$ V, t_1-$t_w = 3200$ s. Marker green square: $Y_{nom} = 10$, $E_1 = -0.2391$ V, t_1-$t_w = 1600$ s, $E_2 = -0.06$ V, $Y_2 = 8.3\times10^{-9}$.

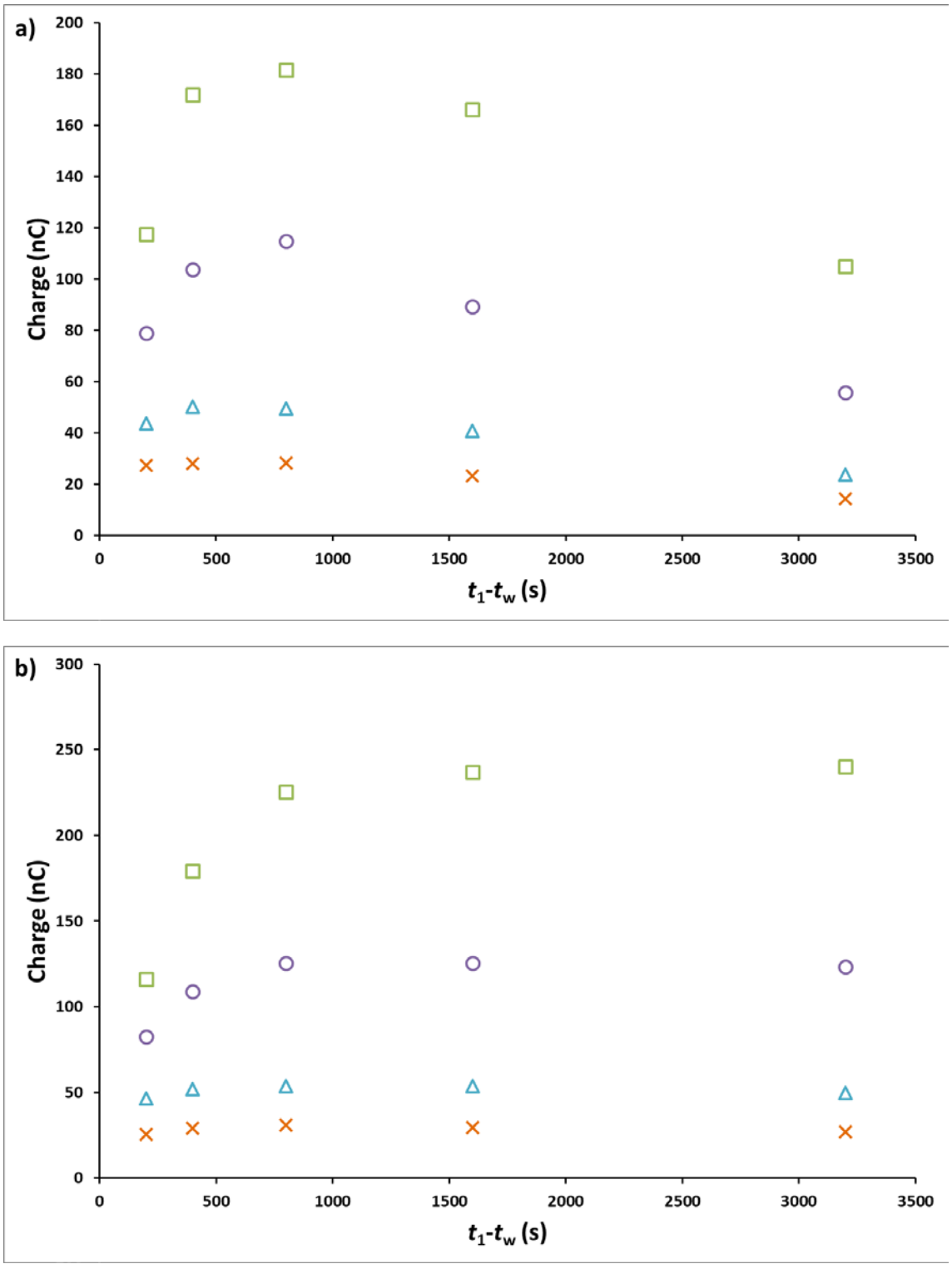
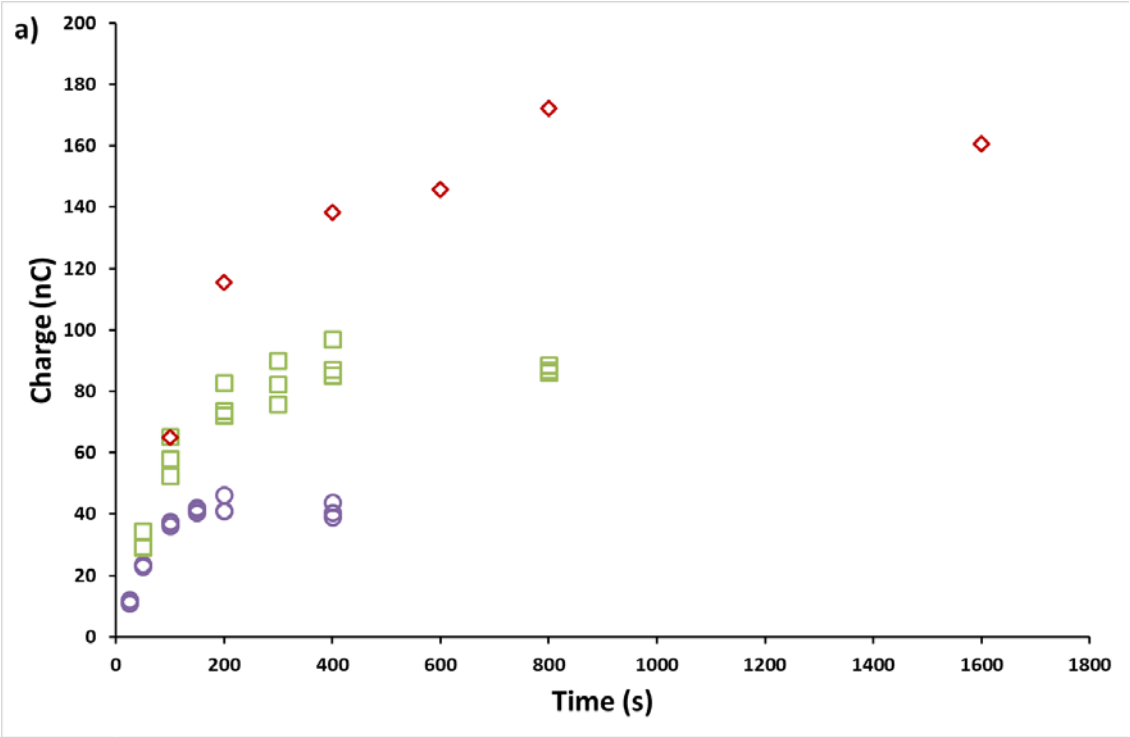


Figure 3. Trajectories of total charge at different gains with AGNES-Q and different integration times in the stripping stage. a) t_2 = 50 s. b) t_2 = 200 s. Orange cross stands for Y_{nom} = 1; E_1 = -0.2194 V. Blue triangle for Y_{nom} = 2; E_1 = -0.2253 V. Lilac circle for Y_{nom} = 5; E_1 = -0.2331 V. Green square for Y_{nom} = 10; E_1 = -0.2391 V. Experimental conditions: $c_{T,Sb}$ = 5×10^{-7} M at pH = 2.053; E_2 = -0.06 V and Y_2 = 8.3 ×10^{-9}.



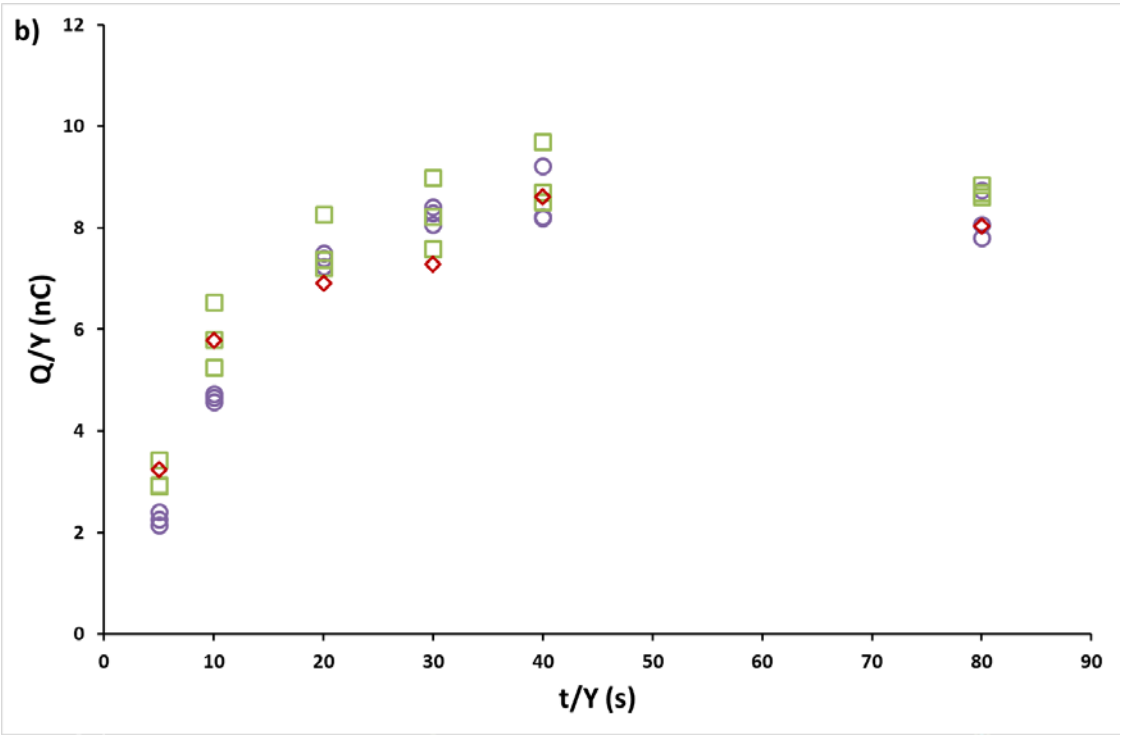


Figure 4. Trajectories at different gains with AGNES-SCP. a) Charge vs. deposition times. b) Normalized charge vs. normalized time. Experimental conditions: $c_{T,Sb}$ = 2×10^{-6} M at pH = 2.078. Lilac circle for Y' = 5; E_1 = -0.1987 V. Green square for Y' = 10; E_1 = -0.2046 V. Dark red diamond stands for Y' = 20; E_1 = -0.2106 V.

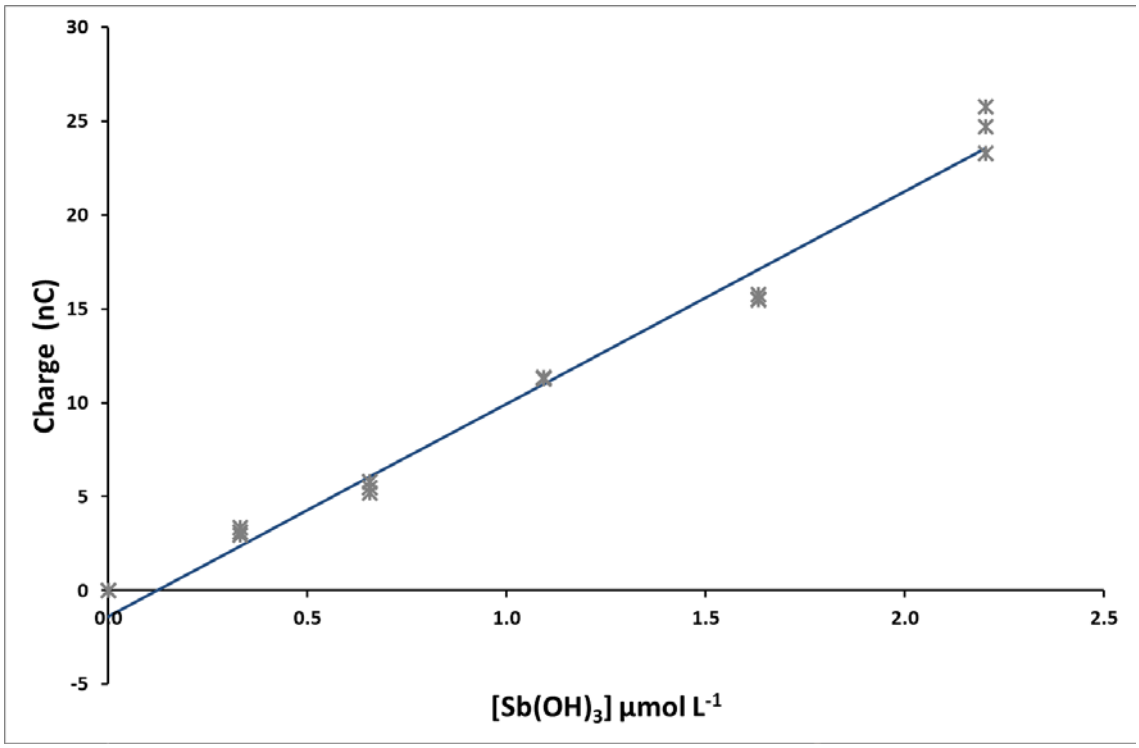


Figure 5. Calibration of Sb for faradaic charges measured with AGNES-SCP vs. [$Sb(OH)_3$]. $Y'_{calib} = 3.64$ was derived from the slope. Experimental conditions: E_{calib} = -0.190 V, t_1 = 200, 300 and 400 s, pH = 1.990 - 2.008.

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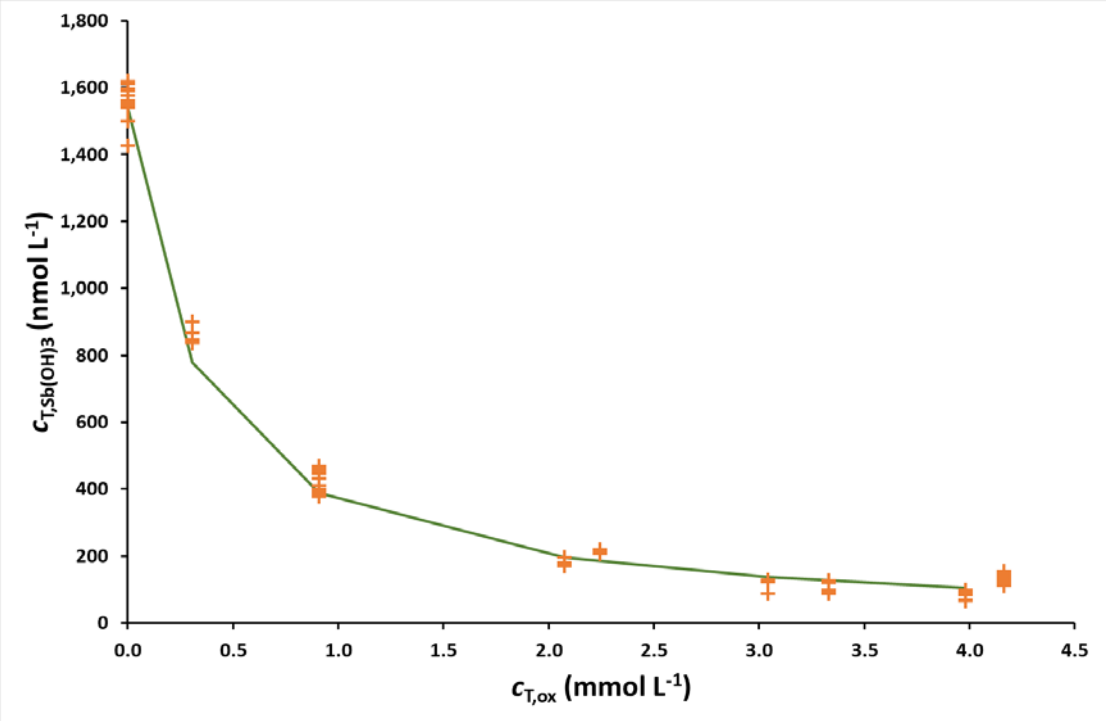

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554 Figure 6.[$Sb(OH)_3$] experimentally determined with AGNES for an initial total Sb
555 concentration of 2×10^{-6} mol L^{-1} and different additions of oxalate at pH = 2.0. Green
556 continuous line stands for VMINTEQ predictions. Orange markers stand for AGNES
557 measurements. Used gains: 3.95, 6.04, 7.10, 10.80 and 16.00. t_1 = 200 and 400 s.